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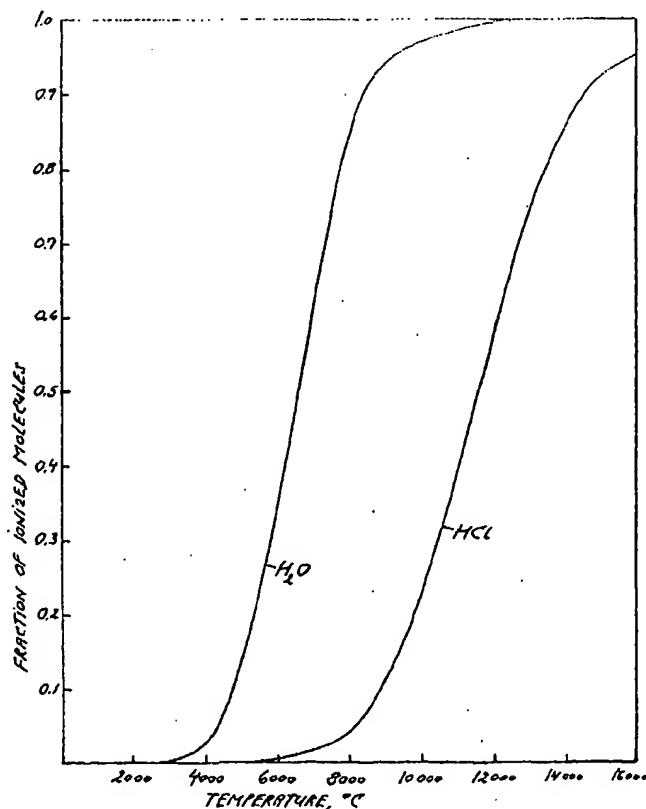
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- (71) Applicants (*for all designated States except US*): **BUZ-ZARD, Jonathan, Leighton** [ZA/ZA]; 38 St. Kilda Avenue, 4001 Durban, Kwa Zulu Natal (ZA). **STEINER, Philipp, D.** [ZA/ZA]; Fleur de Lys, 59 Everton Road, Kloof, 3600 Kwa Zulu Natal (ZA).
- (72) Inventor: **ZEITSCH, Karl, J.** (deceased).
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[Continued on next page]

(54) Title: **GASEOUS ACID CATALYSIS**



The thermal ionization of water vapor and hydrogen chloride vapor at atmospheric pressure.

(57) Abstract: A method of gaseous acid catalysis which finds particular applications in the manufacture of furfural includes the steps of introducing a solid reactant containing one or more hydroxyl groups into a reactor (1); introducing superheated steam from a superheater (2) until the temperature within the reactor (1) is higher than that of the dew points of both water and the catalyst and the reactant is dry. The catalyst is then introduced into the superheated steam by vaporiser (3). Product gas formed is liquified in condenser (4) and the condensate collected in a buffer tank (5). Separation plant 6 isolates the product gas and recovers the acid catalyst, preferably as its azeotrope with water, and recycles it into the vaporiser.

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- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

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## GASEOUS ACID CATALYSIS

### TECHNICAL FIELD OF THE INVENTION

This invention relates to gaseous acid catalysis and in particular gaseous acid catalysis of the conversion of pentose or pentosan to furfural.

### 5 BACKGROUND ART

Acid catalysis, a common reaction mechanism in organic chemistry, implies the involvement of oxonium, or hydronium, ions,  $\text{H}_3\text{O}^+$ . "Acid catalysis" is inherently understood to be a process that occurs in aqueous solution. As far as the applicant is aware nobody seems to have used a gas as an acid catalyst, and with good reason. As  
10 shown in Figure 1, gases are not ionized until very high temperatures are reached. As can be seen, there is no significant thermal ionization below  $2500^\circ\text{C}$  for water and below  $5000^\circ\text{C}$  for HCl. Ionization by cosmic rays and ambient radioactivity has also been shown to be negligible, together amounting to no more than 10 ion pairs/(s  $\text{cm}^3$ ) with a life span of 70 s. Thus, gases at all but extremely high temperatures may be considered completely  
15 nonionized, as demonstrated by their being perfect electrical insulators.

Obviously, a nonionized gas cannot be an "acid catalyst", therefore, it has been the universal belief that acid-catalyzed processes must be carried out in the liquid phase. However, recent studies of stratospheric chemistry and the depletion of the ozone layer have shown that HCl vapour, usually stable, becomes ionized in the presence of ice crystals  
20 that are abundant in the stratosphere. HCl and water vapour molecules are strongly adsorbed on the surface of the ice crystals. In the state of adsorption, each HCl molecules reacts preferentially with four water molecules to form an ionized cluster,  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3\text{Cl}^-$ , in which the three water molecules form the equatorial plane of a trigonal bipyramid, with  $\text{Cl}^-$  and  $\text{H}_3\text{O}^+$  ions at the apexes. The chlorine atom carries a charge of  $-0.80 e$  and the  
25 oxonium ion a charge of  $+0.85 e$ , so that the electrical activity of the cluster is almost equal to that of free  $\text{Cl}^-$  and  $\text{H}_3\text{O}^+$  ions. The role of the solid surface is to permit HCl molecules

to come into contact with four water molecules, which is not possible via collisions in a gas phase devoid of adsorbing surfaces.

It is therefore one object of this invention to provide a method for gaseous acid catalysis.

5       The applicant has further noted the similarity between ice crystals and other solids having multiple polar hydroxyl groups, for example sugars, and in particular pentose or pentosan.

It is therefore a further object of this invention to provide a method for gaseous acid catalysis catalysed hydrolysis of sugars to form aldehydes and in particular, pentosan and  
10   pentose to furfural.

### ***DISCLOSURE OF THE INVENTION***

According to the invention, a method of gaseous acid catalysis includes the steps of introducing a reactant in solid form into a reactor, the reactant including one or more hydroxyl groups; introducing superheated steam into the reactor until the reactant is dry  
15   and the temperature within the reactor is above that of the dewpoints of both water and the catalyst to be used; introducing the acid into the reactor together with the superheated steam by means of a vaporiser; and condensing the gas formed.

In the preferred form of the invention, the reactant is capable of forming an ionised cluster complex with water and at least a portion of the acid.

20       Also in the preferred form, the reaction is carried out at atmospheric pressure. The reactant should be completely dry. In the preferred form, the acid is hydrochloric acid.

In this form of the invention, the reaction must be carried out at a temperature above the boiling point of the maximum HCl - H<sub>2</sub>O azeotrope. This typically occurs at

20.2 wt% of HCl with a boiling point of 108,6°C and accordingly the reaction should be carried out above this temperature.

In one form of the invention, the reactant is a sugar.

In one form of the invention, the reactant is pentosan and/or pentose and the solid  
5 substance is a comminuted raw material high in pentosan content, for example sunflower stems, corn cobs or bagasse.

### ***DESCRIPTION OF AN EXAMPLE OF THE INVENTION***

A typical gaseous acid catalysis process using hydrochloric acid is illustrated in Figure 2. Reactor 1 is charged with comminuted raw material of high pentosan content,  
10 such as sunflower stems, corncobs, or bagasse. Steam at atmospheric pressure is passed through a superheater 2 typically fuelled by combustion gas, and this stream is then passed through the charge to first completely dry the charge and then heat it to a temperature far above the maximum atmospheric dew point of hydrochloric acid. The charge will heat rapidly once the moisture has been stripped from it. When the desired temperature is  
15 reached, a small quantity of hydrochloric acid is continuously dispersed into the superheated stem by means of a vaporizer 3 to give the gas stream an HCl content of approximately 1.5 wt%. The gas stream leaving the reactor is liquefied in a condenser 4, and the condensate is collected in a buffer tank 5 before it enters a separation plant 6 that isolates furfural, low boiling compounds, and carboxylic acids and recovers HCl as its  
20 azeotrope with water. This hydrochloric acid is used to feed the vaporiser 3, so that the catalyst is contained in a closed circuit. The "pervaporisation" of the charge is continued until no more furfural is produced. Then, the residue is discharged under nitrogen, to prevent self-ignition, and a new batch is started.

When this reaction is carried out at 155°C, the applicant found that the existing gas  
25 stream was heavily loaded with furfural, low boiling compounds and carboxylic acids.

What is most surprising about this result is the presence of the furfural as a gas even though the process is carried out at a temperature below its boiling point (161.7°C).

An important advantage of this new process is that the absence of a liquid phase greatly increases the furfural yield. In convention furfural process, the furfural generated  
5 dissolves in the liquid phase, where, under the catalyzing influence of oxonium ions, it undergoes loss reactions with itself and with intermediates of the pentose-to-furfural conversion. In addition, with sulphuric acid as the customary catalyst, there are losses by sulfonation. Consequently, the yield in conventional furfural plants is only on the order of 50%. By contrast, in gaseous acid catalysis, with no liquid phase in which to dissolve,  
10 the generated furfural is instantly vaporised and loss reactions are avoided.

In a laboratory test, yields of the order of 95% have been achieved.

In conventional furfural processing, high pressures are needed to keep the aqueous catalyst in the liquid state, and the customary catalyst, sulphuric acid, is nonvolatile, so that it is lost in the residue where it presents a disposal problem.

15 As compared to this conventional processing, the new gaseous catalysis process has the following advantages :

- 1 At any chosen temperature, the process can be carried out at atmospheric pressure.
2. As the  $H_2O/HCl$  catalyst is used far above its dew point, there is no corrosion, so that the reactor can be made of mild steel.
- 20 3. The acid portion of the catalyst can be completely recovered, to be run in a closed circuit, so that there is no acid consumption and no acid disposal problem. Known technology is available for the acid recovery.
4. The residue is dry and free of acid, thus being eminently suited for a simple combustion without any problems. By partial combustion in air, it is also possible

to use the residue for the manufacture of "producer gas" consisting mostly of carbon monoxide, hydrogen and nitrogen.

5. The yield is close to 100 percent as there is no liquid phase where loss reactions could take place. Yields of up to 95.8 percent have been measured.
- 5 It should be noted that although an example of a batch process is described hereinabove, the applicant submits that a continuous process may be used.

**CLAIMS:**

1. A method of gaseous acid catalysis characterised in that it includes the steps of introducing a reactant in solid form into a reactor, the reactant including one or more hydroxyl groups; introducing superheated steam into the reactor until the reactant is dry  
5 and the temperature within the reactor is above that of the dewpoints of both water and the catalyst to be used; introducing the acid together with the superheated steam into the reactor by means of a vaporiser; and condensing the gas formed.
2. A method according to claim 1 characterised in that the reactant is capable of forming an ionised cluster complete with water and at least a portion of the acid.
- 10 3. A method according to claim 1 or claim 2 characterised in that the reaction is carried out at atmospheric pressure.
4. A method according to any of the above claims characterised in the acid is hydrochloric acid.
5. A method according to claim 4 characterised in that the reaction is carried out at a  
15 temperature above the boiling point of the maximum HCl - H<sub>2</sub>O azeotrope.
6. A method according to claim 1 characterised in that the reactant is a sugar.



7. A process for the manufacture of aldehydes from sugars characterised in that the hydrolysis of the sugar is catalysed by a method of gaseous acid catalysis according to claim 1.
8. A process for the manufacture of furfural from pentosan according to claim 7  
5 characterised in that the hydrolysis of pentosan and/or pentose and subsequent dehydration to furfural is catalysed by gaseous hydrochloric acid according to the method of catalysis of claim 1.
9. A process for the manufacture of furfural characterised in that the hydrochloric acid is recycled as its azeotrope with water.
- 10 10. A process for the manufacture of furfural according to claim 7 characterised in that the reaction is carried out at 155°C.
11. A process for the manufacture of furfural according to claim 7 characterised in that the yield of furfural is greater than 90%.
12. A process according to claim 7 characterised in that it is continuous.

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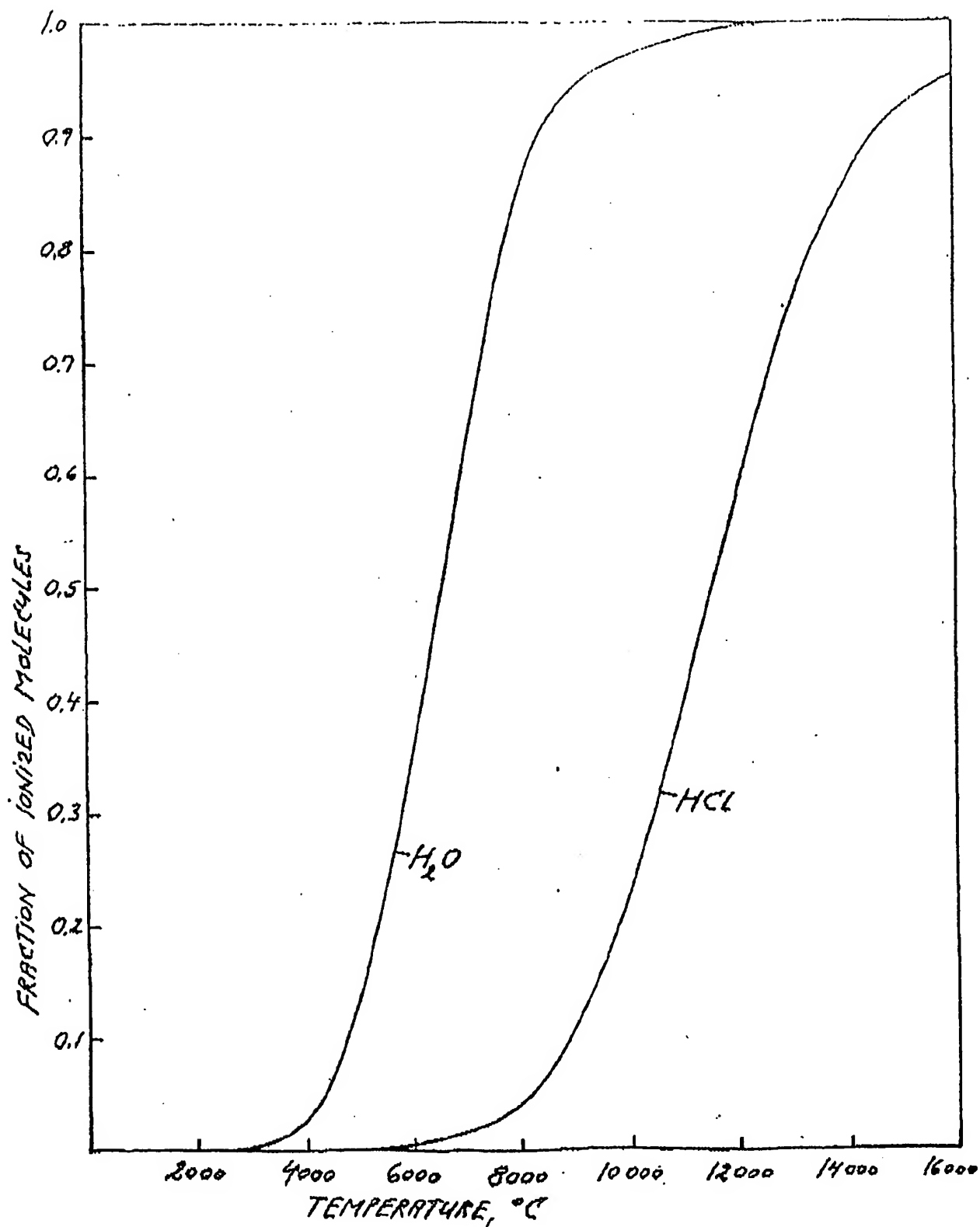


Figure 1. The thermal ionization of water vapor and hydrogen chloride vapor at atmospheric pressure.

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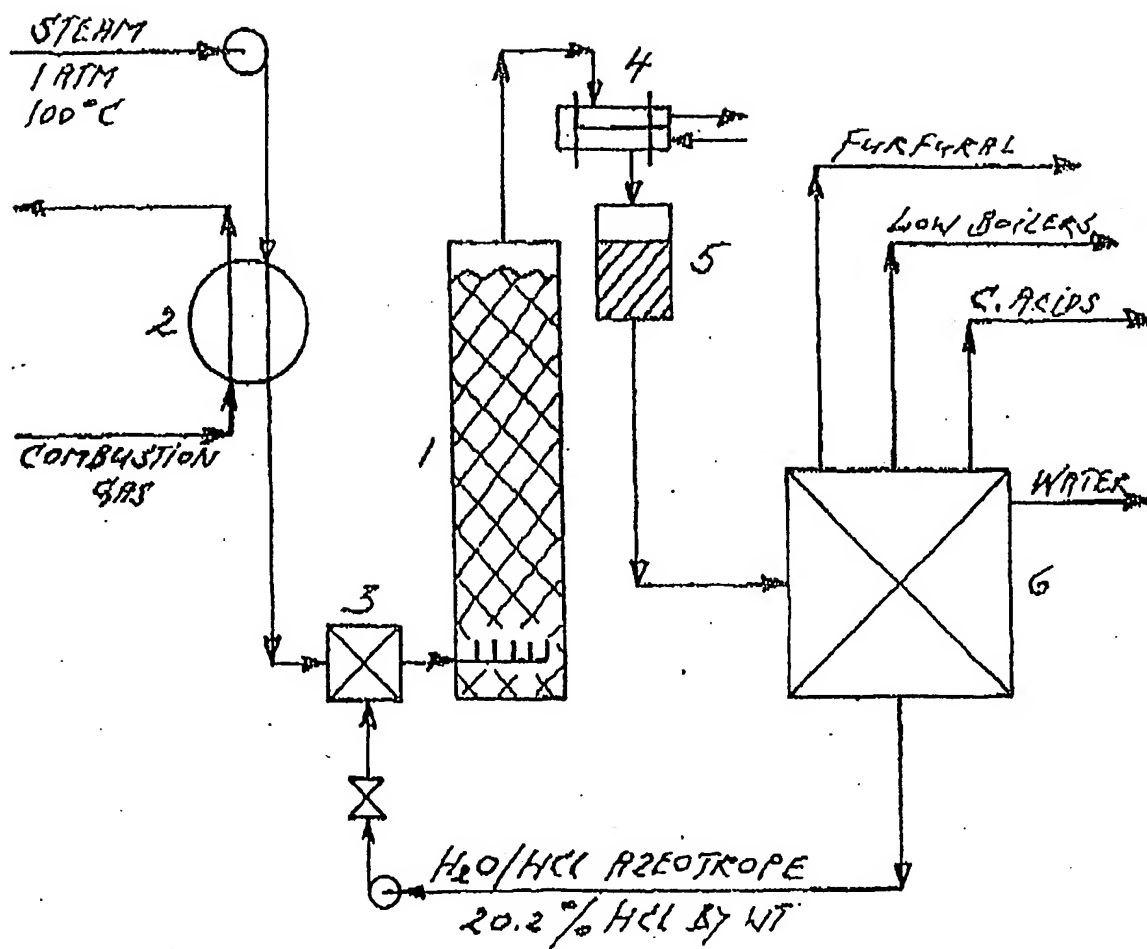


Figure 2. Illustration of a gaseous acid catalysis.

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C07D307/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 001 283 A (WELLS JR PRESTON A) 4 January 1977 (1977-01-04) column 1, line 7 -column 1, line 10; claim 4; examples 1,2	6-12
A	US 4 154 744 A (HAMADA KAZUHIKO ET AL) 15 May 1979 (1979-05-15) column 1, line 64 -column 2, line 35; claims 1-9; examples 1-13	6-12

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

5 February 2002

Date of mailing of the international search report

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Name and mailing address of the ISA  
European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
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## FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1-5

Present claims 1-5 relate to an extremely large number of possible methods respective compounds to be prepared with. Support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the claimed methods and compounds to be prepared with. In the present case, the above claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely claims 6-12.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
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